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Order-disorder transitions in self-assembled polymers: A positron annihilation study

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We report here the first results of order-disorder transition (ODT) in a self-assembled comb-like polymer-amphiphile supramolecular system as identified from the change in positron lifetime parameters. We have used poly(4-vinyl pyridine) hydrogen bonded with 3-pentadecyl phenol, which upon heating showed a stepwise reduction in *o*-Ps intensity at the ODT from lamellar self-assembled state to the disordered state. The ODT temperature was confirmed by differential scanning calorimetry and small angle X-ray scattering. The free volume "holes" in this polymer-amphiphile system are proposed to be near the chain ends of the polymer backbones. We suggest that positron lifetime spectroscopy can serve as a technique to identify ODTs in self-assembled lamellar structured supramolecular systems.

1 Introduction It is expected that new functional materials and technologies are based on self-assembled polymers and hence deeper understanding on these materials at all length scales employing various characterisation techniques becomes essential. In the case of block copolymers, the covalently bonded but mutually repulsive blocks lead to microphase separation and forms various self-assembled nanostructures [1,2]. If the blocks are not too repulsive, a transition from an ordered state to a disordered state can be observed by heating past an order-disorder transition temperature (T_{ODT}) [3]. Polymer-amphiphile systems with comb-shaped architecture tend to self-organise in essentially similar way to that of block copolymers [2]. Upon heating, polymer-amphiphile systems also show an order-disorder transition (ODT), which depends on the polar-nonpolar repulsion [2,4]. Polymer-amphiphile complexes can also be included as blocks in block copolymers, thus allowing hierarchical self-assemblies and the related phase transitions lead to materials with thermo responsive electrical and optical properties [2].

The commonly employed techniques to identify ODTs in polymer includes small angle X-ray scattering (SAXS), small angle neutron scattering (SANS), transmission electron microscopy (TEM), differential scanning calorimetry (DSC), polarized optical microscopy (POM) and dynamic mechanical spectroscopy (DMS). It has been suggested in diblock copolymers that free volume is increased to screen the unfavourable interactions between the repulsive blocks [5]. Here we introduce positron annihilation lifetime spectroscopy (PALS) as a method to directly probe the free volume changes related to order-disorder transitions in self-assembled systems. As model system, poly(4-vinyl pyridine) (P4VP) hydrogen bonded with 3-pentadecyl phenol (PDP) was chosen, since its self-assembly and ODT are well documented [4].

2 Experimental

2.1 Complex preparation The polymer, poly(4-vinyl pyridine) with two different molecular weights M_n = 5100 g/mol (denoted as LMW-P4VP, procured from polymer source, Inc., Canada) and M_n = 30,000 g/mol (denoted as HMW-P4VP, obtained from Polysciences Ltd) are used as procured. The amphiphile 3-pentadecyl phenol (PDP) was obtained from Aldrich (purity 98%) and was further purified by recrystallizing twice from petrol ether. The complex P4VP(PDP)$_x$ was prepared by evaporating from DMF solution [4]. Here, the subscript x refers the nominal number of PDP molecules per repeat unit of P4VP and we have selected x = 0.9 to minimize the fraction of unbound PDP [4].

2.2 Characterization techniques The SAXS measurements were done with a system which consists of a 2-D area detector (Bruker AXS) and a Bruker MICRO-STAR rotating X-ray source with Montel optics (Cu K_α radiation, λ=1.54 Å). The DSC measurements were performed using a Mettler DSC-821 using a heating rate of 10 ^{o}C/min and a nitrogen purge flow of 80 ml/min. The PALS was performed using a conventional fast-fast coincidence system having a time resolution of 0.270 ns (full width at half maximum) determined from ^{60}Co prompt spectrum. A ^{22}Na positron source with an activity of 8 μCi was deposited and sealed between two thin aluminium foils. Two nearly circular discs (diameter ~ 12 mm, thickness ~ 0.8 mm) were molded of P4VP(PDP)$_{0.9}$ by pressing between two Teflon sheets and were mounted on both the sides of the positron source to form a sample-source-sample sandwich arrangement. The samples were heated with a resistive heating system with a heating rate of 5 ^{o}C/min. Positron lifetime spectra with more than one million counts were accumulated at each temperatures and the lifetime spectra were analyzed using PATFIT-88 [6].

Using three component analysis, the *o*-Ps lifetime (τ_3) and its intensity (I_3) are obtained and attributed to the pick-off annihilation of *o*-Ps localised in the free volume holes. To calculate the average hole size, we have used the so-called "standard model" [7] where it is assumed that *o*-Ps is confined in an infinitely deep spherical potential well of radius R and the relation between τ_3 and R is given as

$$\tau_3 = 0.5[1-(R/R_o)+(1/2\pi)\,\mathrm{Sin}2\pi(R/R_o)]^{-1}\ \mathrm{ns} \qquad (1)$$

with R_0 = R+ΔR and ΔR = 0.1656 nm [7]. Using the value of R, the average free volume hole size at each temperature is calculated as $V_{f3} = (4/3)\,\pi R^3$.

3 Results and discussion The phenolic group of PDP is involved in the hydrogen bonding with the pyridine nitrogens of P4VP which results in a self-assembled lamellar structure with alternating non polar layers of pentadecyl tails and polar layers of pyridine groups and phenolic heads of the amphiphiles [4]. In the case of LMW-P4VP(PDP)$_{0.9}$, (Figs. 1A and B) the DSC shows an endothermic peak at ca. 54 ^{o}C (Fig, 1B, inset) and SAXS indicates that the complex has lamellar structure with a periodicity of 38 Å that disappears upon passing 55 ^{o}C. The optical birefringence of the material (observed with an optical microscope) is lost also at this temperature. The lamellar structure and the birefringence are reversibly recovered upon cooling. From these measurements, it is clear that there is an order-disorder transition temperature (T_{ODT}) for LMW-P4VP(PDP)$_{0.9}$ at ca. 55 ^{o}C. Interestingly, PALS results (both τ_3 and I_3) show an abrupt change at ca. 55 ^{o}C and the initial values are recovered upon cooling back to room temperature within the experimental data scatter. The free volume holes size (calculated as per equation 1) remains almost constant at ca. 180 Å^3 up to 55 ^{o}C and shows a stepwise decrease thereafter. It is known in polymers that the free volume gets reduced upon degradation [8]. A separate thermo gravimetric analysis (TGA) measurement do not show significant weight loss at this temperature thus revealing that the free volume reduction is not due to thermally induced degradation. This suggests that PALS is sensitive to ODT in self-assembled lamellar structured supramolecular systems.

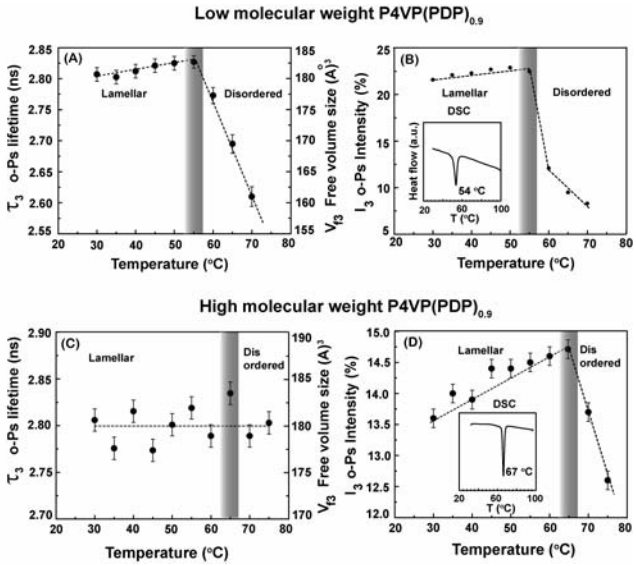

Figure 1 (A) The *o*-Ps lifetime (τ_3) and free volume hole size (V_{f3}) and (B) *o*-Ps intensity (I_3) as a function of temperature for LMW-P4VP(PDP)$_{0.9}$ and (C) and (D) show the corresponding plots for the high molecular weight complex HMW-P4VP(PDP)$_{0.9}$. The order-disorder transition regions are marked by grey bands. The dotted lines are drawn only to guide the eyes. The insets in (B) and (D) show the DSC plots.

We next discuss the results of HMW-P4VP(PDP)$_{0.9}$ (Figs. 1C and D). The DSC shows an endothermic peak on passing 67 ^{o}C (Fig. 1D, inset). Similar to the low molecular weight complex, SAXS measurement of HMW-P4VP(PDP)$_{0.9}$ reveals lamellar structure with almost the same periodicity that disappears at ca. 65 ^{o}C as well as the optical birefringence is lost at this temperature. This reveals that the T_{ODT} of this complex to be 65 ^{o}C. The o-Ps

intensity (I_3) for this complex shows a small increase up to 65 °C and is stepwise reduced on passing T_{ODT}. But, the relative decrease in I_3 value is considerably smaller in this case as compared to low molecular weight complex. The stepwise drop of I_3 values both for LMW-P4VP(PDP)$_{0.9}$ and HMW-P4VP(PDP)$_{0.9}$ takes place at their respective T_{ODT}s also demonstrates that the changes in PALS parameters are indeed related to the ODT. But in contrast to the low molecular weight complex, the high molecular weight complex does not show a clear change in free volume hole size (V_{f3}) at T_{ODT} taken the scatter of the data.

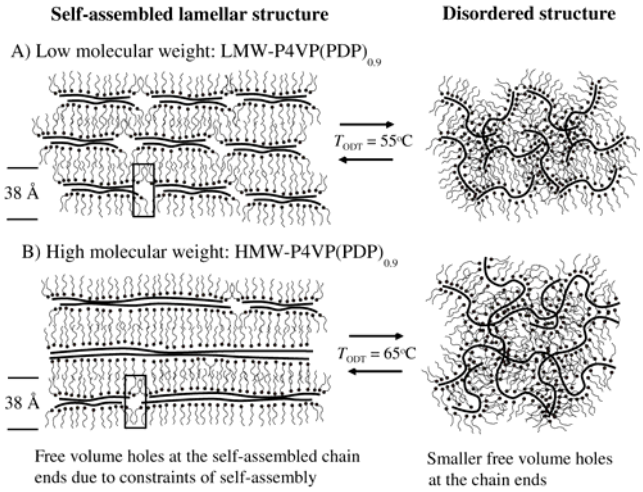

Figure 2 A) Schematic representation of the proposed lamellar structure of P4VP(PDP)$_{0.9}$ suggesting a large population of free volume "holes" (as resolved by PALS) near the chain ends of self-assembled low molecular weight complex in comparison with its disordered state. B) For high molecular weight complex, there is smaller number of free volume holes at the chain ends. Examples of free volume holes at the chain ends within the lamellar self-assemblies have been indicated using boxes.

The decreased *o*-Ps intensity in both the complexes above T_{ODT} reveals reduced pick-off annihilation rate in the disordered state. Now, it becomes interest to understand the possible location of these surprisingly large free volume holes (size 180 Å^3) in these self-assembled comb-like polymer-amphiphile complexes, in an effort to infer the possible sites of *o*-Ps pick-off annihilation. As the two complexes differ only in terms of molecular weight of the polymer, the I_3 values of the two complexes suggest that the fraction of P4VP chain ends play an important role in relation to the pick-off annihilation at ODT (see schematic Fig. 2). For the low molecular weight complex, there is a higher fraction of such self-assembled chain end free volume "holes" expected thus qualitatively explaining why I_3 for LMW-P4VP(PDP)$_{0.9}$ is much higher than that of HMW-P4VP(PDP)$_{0.9}$. In the disordered state, the chain ends can more freely adjust to fill the cavities, which leads to less efficient *o*-Ps formation.

Free volumes within the self-assembled block copolymers have previously been considered where excess free volume is suggested for domains which are rich in more compressible constituent [5]. If there is no compressibility difference between the blocks, then the excess free volume is expected to be present at the interface between the two compressible polymers in order to screen the unfavourable interactions [9]. Extending the above concepts to the present comb-like polymer complexes having a self-assembled lamellar structure, one would expect that the free volume may arise from three regions i) more flexible alkyl tail regions ii) interface between the polar and non-polar regions involving hydrogen bonding iii) backbone polymer chain ends. In the first case, i.e., assuming the alkyl chain domains have much higher compressibility, free volume size of 180 Å^3 is less realistic as the alkyl tails are interdigitated (see schematic Figure 2). On the other hand, if one argues that the compressibility difference between the polar part and the non polar alkyl tail is not large, then it is possible that the free volume can originate at the interface between the polar backbone and the non-polar alkyl tail. But based on the previous studies in polar polymers, it is known that positronium (Ps) prefers large open spaces than polar sites [10]. These arguments further support the hypothesis that the main free volume contribution and ODT effects as resolved in PALS are due to chain ends.

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